

Buckling characteristics of multiwalled carbon nanotubes under external pressure

Motohiro Sato[†]

*Department of Socio-Environmental Engineering, Graduate School of Engineering,
Hokkaido University, Sapporo, Japan*

Hiroyuki Shima[‡]

Department of Applied Physics, Graduate School of Engineering, Hokkaido University, Sapporo, Japan

(Received May 14, 2009, Accepted May 23, 2009)

Abstract. This article describes recent work on mechanics of *carbon nanotubes*, one of the most fundamental and amazing man-made nanostructures. The noteworthy point is that “nano”-scale mechanics of carbon nanotubes can be well described by the continuum elastic theories for “macro”-scale thin shells. This provides an efficient means to elucidate mechanical deformation effects of carbon nanotubes on their physical and chemical properties, which is significant to develop new-generation nanomaterials based on nanotubes and their composites. Potential applications of the mechanical deformation of nanotubes in nano-electronics and nano-biology are also commented. In addition, theoretical investigations regarding external pressure buckling is carried out here and we have numerically confirmed that larger N (the number of layers) and a smaller D (the innermost diameter) make “corrugation modes” with a larger mode-index k be energetically favored.

Keywords: carbon nanotube; elastic deformation; buckling; high pressure.

1. Introduction

Nanostructure science is widely believed to spark technological innovation in the next decades. Recent advances in nano-processing techniques have enabled to fabricate various kinds of nanostructures with novel geometry, most of which exhibit unprecedented properties not seen in macroscopic structures. Among such nanostructured materials, carbon nanotubes have drawn great deal of attention. Carbon nanotubes, originally discovered by S. Iijima (1991), are nano-scopic “tubes” made of rolled-up two-dimensional carbon sheets. The outer diameters are within the range from a few to several tens nanometers, and lengths of up to one micrometer. Most striking is the fact that they have unique, excellent mechanical properties. Indeed, carbon nanotubes possess extremely high Young’s modulus of the order of TPa (i.e., several times stiffer than steel), and tensile strengths as high as tens of GPa. Due to the large stiffness, the axial thermal conductivity

[†] Assistant Professor, Corresponding author, E-mail: tayu@eng.hokudai.ac.jp

[‡] Assistant Professor, E-mail: shima@eng.hokudai.ac.jp

becomes higher than even that of diamond. Besides, carbon nanotubes are known to have enormous flexibility for bending, which allows reversible deformation under axial compression. These unusual mechanical properties make carbon nanotubes an ideal material for superstrong nano-fiber, thus holding great promise for synthesizing next-generation materials.

To fully profit by the large potential of carbon nanotubes, it is crucial to establish a fundamental understanding of the structural property. In this article, we give an overview of recent progress in modeling the mechanical properties of carbon nanotubes. Particularly interesting is the fact that, despite of difference in scale, the “nano”-scale mechanics of nanotubes can be successfully described by the well-established elastic theories for “macro”-scale thin shells. This means that mechanical deformation such as buckling and stretching, commonly observed for macroscopic thin shells, occurs in carbon nanotubes. Some potential applications of the mechanical deformation of nanotubes in nanotechnology will be also discussed.

2. Microscopic structure of nanotubes

2.1 Single-Walled and Multi-Walled Nanotube

Carbon nanotubes are large macromolecules established by many carbon atoms, having long and thin cylindrical shape (See Fig. 1). As seen in the figure, it is composed of a graphite sheet (*i.e.*, two-dimensional hexagonal lattices of carbon atoms) rolled up into a cylinder, which looks like a rolled-up sheet of “chicken wire”. This intriguing structure has sparked much excitement in the recent years, and a large amount of research has been dedicated to their understanding. Nevertheless, physical properties of nanotubes are still to be discovered and disputed. What makes it so difficult is that nanotubes have a very broad range of electronic, thermal, and structural properties that alter depending on their geometric character such as diameter, length, and so on.

The original carbon nanotubes discovered in 1991 by S. Iijima were multi-walled carbon nanotubes having outer diameters in the range of 4-30 nm, and lengths of up to 1 μm . A multi-walled nanotube is a seamless cylindrical object composed of multiple concentric shells. Each concentric shell is made of a rolled-up graphite sheet, and is separated from each other by an inter-shell spacing of 3.4 \AA . In 1993, the fundamental form of the nanotubes depicted in Fig. 1, called “single”-walled carbon nanotubes, was also synthesized from graphite. Most single-walled nanotubes have a diameter of close to 1 nm, with a tube length that can be many thousands of times longer than the diameter. It was also revealed that single-walled nanotubes can aggregate to form bundles, normally arranged in hexagonal formations that constitute nanocrystals of carbon

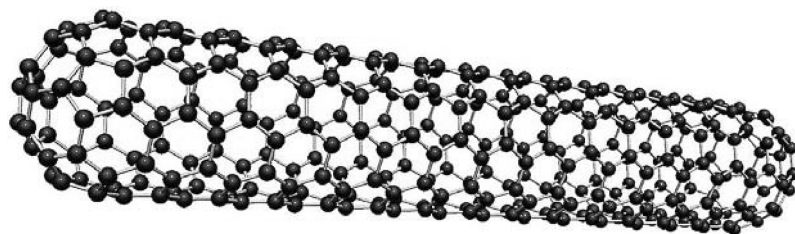


Fig. 1 Microscopic structure of a single-walled carbon nanotube. It consists of a large number of carbon atoms, having long and thin cylindrical shape with a hemispherical “cap” at each end of the cylinder.

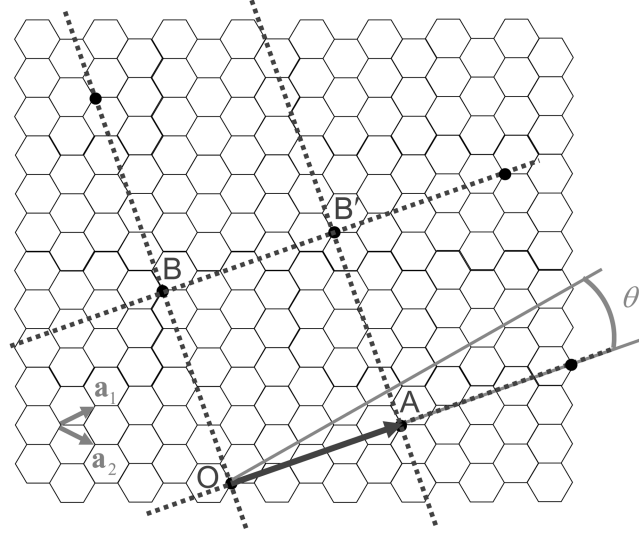


Fig. 2 An illustration of the (n, m) nanotube naming scheme. (a) A chiral vector $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$ assigned on an infinite graphene sheet describes how to “roll up” the sheet to make a cylindrical nanotube. Here \mathbf{a}_1 and \mathbf{a}_2 are the unit vectors of the hexagonal lattice, and the chiral angle θ is measured relative to the direction defined by \mathbf{a}_1 . To form the nanotube, imagine that the square region bounded by OAB'B is rolled up so that O meets A and B meets B'; the resulting carbon nanotubes is referred to as a type of $(n, m) = (4, 1)$. Different types of carbon nanotubes have different values of n and m . If $m = 0$, the nanotubes are called “zigzag” with a chiral angle of 0° . If $n = m$, the nanotubes are called “armchair” with a chiral angle of 30° . Otherwise, they are called “chiral”, whose chiral angles are between 0° and 30° .

nanotubes. The structure of these nanocrystals closely mimics that of porous materials, with nanometer spaces available both inside the tubes and also in the interstitial spaces between them.

2.2 Chiral Vector of a Nanotube

Following the notation of White *et al.* (1993), each single-walled nanotube is indexed by a pair of integers n and m . These two integers define the so-called chiral vector expressed by

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \quad (1)$$

where \mathbf{a}_1 and \mathbf{a}_2 are unit vectors of a two-dimensional hexagonal lattice of carbon atoms (See Fig. 2). When the graphene sheet is rolled up to form a nanotube, the ends of the chiral vector meet each other. The chiral vector thus forms the circumference of the nanotube's circular cross-section. It also follows that the diameter D of a single-walled tube of type (n, m) reads

$$D = \frac{a_{C-C}}{\pi} \sqrt{3(m^2 + mn + n^2)} \quad (2)$$

where a_{C-C} is the distance between neighboring carbon atoms in the flat sheet.

3. Mechanical strength of carbon nanotubes

Nowadays, carbon nanotubes play a significant role as building blocks in many fields of

nanotechnology and nanomaterial engineering. A thorough understanding of their nanomechanics is, therefore, essential when designing nanodevices and nanomaterials. This section devotes to review the recent progress of the issue, particularly focuses on the mechanical strength of carbon nanotubes.

3.1 Tensile Strength

Carbon nanotubes are the strongest and stiffest materials on earth, in terms of tensile strength and elastic modulus. In fact, carbon nanotubes possess remarkable mechanical properties, implying that they are ideal candidates for nanoelectromechanical systems. For example, Young's modulus of nanotubes is estimated to be of the order of TPa, making them the material with the highest tensile strength known by far, capable of sustaining high strains without fracture. The first theoretical prediction of the mechanical properties of carbon nanotubes was done by Overney *et al.* (1993). By using a Keating potential, they have shown that Young's modulus of a single-walled carbon nanotube can be up to 1.5 TPa, which surpasses materials with high tensile strength such as steel strings and synthetic fibers. Other group has used different methods to investigate various mechanical properties of carbon nanotubes (Ruoff and Lorents 1995, Lu 1997, Wong *et al.* 1997, Hernandez *et al.* 1998 and Nardelli *et al.* 1998), which ensure that nanotubes are expected to be resilient materials with remarkably high stiffness.

The first experiment on the Young's modulus of multi-walled nanotubes came from Treacy *et al.* (1996). Young's modulus they obtained was 0.40 TPa being the lowest, and 4.15 TPa being the highest. They found a trend for higher moduli with smaller tube diameters. After that, Poncharal *et al.* (1999) employed electromechanical resonances to measure Young's modulus of multi-walled nanotubes as a function of the diameter. In this experiment, nanotubes were excited at their resonant frequency, which depends on the square root of Young's modulus. A striking decrease of the Young's modulus was observed when the diameter exceeded about 10 nm, in contrast with other static bending experiments. The strong decrease of Young's modulus attributes to the anisotropy of multi-walled nanotubes that induces an unusual dynamical behavior.

3.2 Buckling under compression

Carbon nanotubes are not nearly as strong under compression because of their hollow structure and high aspect ratio. Indeed, it has turned out that carbon nanotubes tend to undergo buckling when placed under compressive, torsional or bending stress. A numerical study was conducted by Yakobson *et al.* (1996, 1997) based on the Tersoff–Brenner potential, which suggested a buckling strain of 0.05 under compression. Buckling due to bending and torsion was also demonstrated in Refs. (Bernholc *et al.* 1998, Qian *et al.* 2003, Arroyo and Belytschko 2003, Natsuki and Endo 2004, Natsuki *et al.* 2004a,b, Hasegawa and Nishidate 2006, Batra and Sears 2007, Jensen *et al.* 2007, Wang *et al.* 2007, Chang 2007, Li *et al.* 2008, Arroyo and Arias 2008, Arias and Arroyo 2008 and Sun and Liu 2008), and is characterized by a collapse in the cross-section which results in a kink or ribbon-like structure. Experimental observations of buckling in carbon nanotubes were made by several groups (Despres *et al.* 1995, Iijima *et al.* 1996, Wong *et al.* 1997, Demczyk *et al.* 2002 and Jensen *et al.* 2007).

A major factor that contributes to the buckling mode is the radial deformability of the tubes. Ruoff *et al.* (1993) experimentally studied a system of two multi-walled nanotubes close to each other, and concluded that nanotubes in anisotropic physical environments (i.e., on a surface or in the vicinity of other objects) are not perfectly cylindrical. This attributes to the van der Waals attraction

between nanotubes, since the attractive force develops an interfacial region. A closest-packed single-walled nanotube crystal was further studied by Tersoff and Ruoff (1994). They found that tubes with diameters smaller than 1 nm are little affected in their geometry by the inter-tube interaction, but that tubes with diameter exceeding roughly 2.5 nm are faceted. Polygonized single-walled nanotubes in contact, and fully collapsed multi-walled nanotubes have been reported by Chopra *et al.* (1995), Benedict *et al.* (1998) and Lopez *et al.* (2001), respectively. Radial deformation of multi-walled nanotubes on a substrate was also investigated by both experiment and simulation (Hertel *et al.* 1998 and Avouris *et al.* 1998), which validate the prediction by the earlier work (Tersoff and Ruoff 1994). Fully or partially collapsed multi-walled nanotubes on surfaces have been reported by Yu *et al.* (2001a, 2001b), which also included an energetic analysis of the contact.

Numerical simulations done by Lordi and Yao (1998) indicated that the radial deformation can be reversible and elastic, depending on the type of carbon nanotube. Through molecular-dynamics simulations, Gao *et al.* (1998) studied the dependence of cross-sectional shape on the isolated single-walled nanotube diameter. They found that the circular shape is stable if the tube radius is less than 1 nm. When the tube radius is between 1 and 2 nm, both near-circular and collapsed shapes are favored. For radius values larger than 3 nm, single-walled nanotubes should collapse to a ribbon. In short, the low dimensional geometry makes structural instability an important issue for the mechanical application of nanotubes. Further study is needed for understanding mechanics in partially or fully collapsed nanotube and nanotube bundles.

4. Continuum elastic theories for nanotubes

Nanomechanical properties of carbon nanotubes have long been modeled via atomistic-based techniques such as molecular dynamics simulations, in which the discrete nature of atomic configuration in the graphene sheet is fully considered. In recent years, however, several types of continuum-based elasticity models have been extensively employed to describe structural properties of both single-walled and multi-walled carbon nanotubes. Surprisingly, the results stemming from the latter approach agree well with those obtained from the atomistic-based studies, although the discreteness of the nanotube structure is ignored in the continuum-based approach. These agreements indicate that the laws of continuum-based elasticity have some relevance and applications in nanoscale domains.

The continuum-based models that have been used so far include the nonlinear thin-shell models, the models based on curved plates, models based on vibrating rods and models of bending beams. For instance, the Euler-Bernoulli beam-bending theory has been applied to the investigation of such mechanical and structural properties of nanotubes as static column-buckling, vibration of multiwall nanotubes, static deflection, sound-wave propagation, resonant frequencies and vibrational modes. Close agreements between the experimental and computational results have been reported.

5. Radial elastic deformation of nanotubes

5.1 Theoretical investigations

Radial deformation of nanotubes under pressure has been intensively studied in the last decade

from both theoretical and experimental viewpoints (Natsuki *et al.* 2004, Hasegawa and Nishidate (2006), Tang *et al.* (2000, 2002), Peters *et al.* (2000), Sharma *et al.* (2001), Rols *et al.* (2001), Reich *et al.* (2002 and 2003), Wang *et al.* (2003), Elliott *et al.* (2004), Tangney *et al.* (2005), Gadagkar *et al.* (2006), Zhang *et al.* (2006), Yang *et al.* (2006) and Christofilos *et al.* (2007)). For instance, Lordi and Yao (1998) studied the mechanical force-structure relationship of carbon nanotubes under asymmetric radial compressive forces by using molecular dynamics simulations. They concluded that the mechanical stiffness of the concentric walls depend on the diameter of the tube and the number of layers. Tube compliance increased as tube diameter increased. Increasing the number of layers for a nominal tube diameter has the effect of stiffening the walls, resulting in harder impacts. Reich *et al.* (2002) conducted an *ab initio* calculation on the effective radial modulus of the nanotube with diameter of 0.8 nm under hydrostatic pressure, which gave a value of 650 GPa. Recently, Li and Chou (2003) studied the elastic deformation of single-walled nanotubes under hydrostatic pressure by using the molecular structural mechanics method, which was developed by linking the molecular mechanics constants of force fields and frame sectional stiffness parameters. The study shows that the effective radial Young's modulus (by viewing the tube as solid cylinder) is highly dependent on the tube diameter. It decreases rather rapidly with increasing tube diameter.

Most of above studies are based on the assumption that the tube is considered as solid cylinder under asymmetrical or hydrostatic pressure. Alternatively, the radial deformation of single-walled nanotubes should be governed by the hoop deformation of a thin hollow tube. This motivates to separate out the contributions of tube geometry and size-dependent hoop modulus on the resistance of single-walled nanotubes to radial pressure.

5.2 Experimental results

Due to the thin hollow structure, a nanotube may collapse when hydrostatic pressure is higher than the critical buckling pressure. Chesnokov *et al.* (1999) experimentally found the radial deformation of single-walled nanotubes with diameters around 1.36 nm is reversible up to 2.9 GPa. After that, it has been observed the radial deformation of a bundle of single-walled tubes with a diameter of 1.4 nm is reversible up to 4 GPa (Tang J. *et al.* 2000). To date, only one experimental result is available (Tang D.S. *et al.* 2000) for critical buckling pressure of a multi-walled nanotube, in which tubes with 20 layers and an innermost diameter of 3 nm were employed to measure the electrical resistance and capacitance under pressure. They observed very little change in the electrical structure of nanotubes induced by high pressure up to 1.4 GPa.

Radial elastic deformation of carbon nanotubes has been investigated experimentally using different test techniques. Shen *et al.* (2000) used a microscope method to investigate the radial compression of multi-walled nanotubes under an asymmetric stress. They observed that the radial compressive modulus increases from 9.7 to 80 GPa when a tube with 10 nm diameter was compressed from 26 and 46% in diameter. Yu *et al.* (2000) have studied the radial deformability of a multi-walled nanotube to observe that the tube with an outermost diameter of 8 nm has values of effective radial modulus (by treating the tube as a uniform and isotropic solid cylinder with a Poisson's ratio of 0.5) ranging from 0.3 to 4 GPa at different sections measured, which are comparable with the Young's modulus values of semi-crystalline polymers.

Beside of asymmetric radial pressure, hydrostatic pressure provides an ideal condition to study the radial deformation of carbon nanotubes. Tang J. *et al.* (2000) have investigated the compressibility and polygonization of single-walled nanotube bundles under hydrostatic pressure by using a

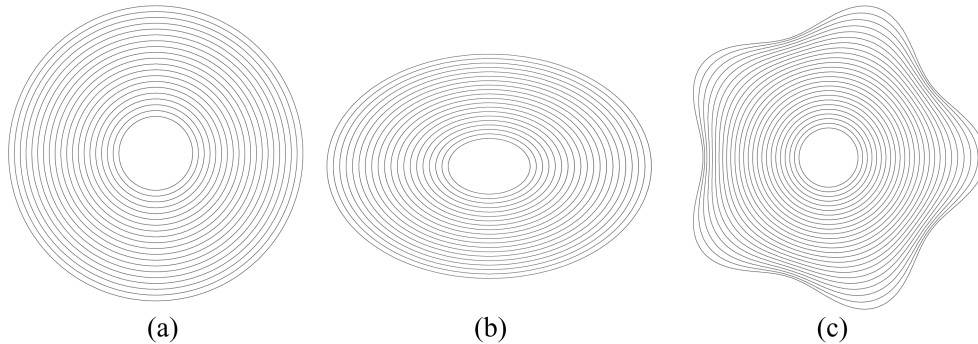


Fig. 3 Cross-sectional views of multi-walled carbon nanotubes under hydrostatic pressure. Typical three kinds of cross-sectional shapes are depicted: (a) a circular shape, (b) an elliptically-deformed one, and (c) a radially-corrugated one. Which kind of deformation mode occurs at high pressure depends on the values of the number of concentric shells N and the innermost tube diameter D .

diamond anvil cell and in situ x-ray diffraction. The volume compressibility of the bundle with the lattice constant of 17.2 \AA and tube diameter of 14.1 \AA was obtained to be 0.024 GPa^{-1} .

6. Radial corrugation of multi-walled nanotubes

In this section, we demonstrate our latest theoretical results as to the radial deformation of multi-walled carbon nanotubes under hydrostatic pressure (Shima and Sato 2008, Shima and Sato 2009). A continuum-based approximation method has been employed to reveal a novel kind of pressure-induced radial deformation, called *radial corrugation*. Such the radial corrugation phenomenon is peculiar to multi-walled nanotubes with the number of constituent wall N be much greater than unity. In a corrugation mode, only a few outermost walls show significant radial corrugation along the circumference direction, while the innermost tube keep its cylindrical symmetry (See Fig. 3). The present results provide useful information in developing nanotube-based nanofluidic (Majumder *et al.* 2002, Noy *et al.* 2007, Whitby *et al.* 2007 and Khosravian 2007, 2008) or nanoelectrochemical devices (Frackowiak and Beguin 2001, 2002 and Kowalczyk *et al.* 2007) for which the geometry in the innermost or outermost tube is significant for their performance. Effects of mechanical deformation and curved geometry on electronic and optical properties of carbon nanotubes, as recently found in low-dimensional materials (Onoe *et al.* 2007, Taira and Shima 2007, Nishio, Balakrishnan and Dandolo 2008, Toda *et al.* 2008, Shima *et al.* 2008, Ono and Shima 2008, Taira and Shima 2009), are also interesting to explore.

6.1 Mechanical Energy Formulation

A stable cross-section shape of a multi-walled nanotube under hydrostatic pressure can be evaluated by using the continuum elastic theory. We assume the 2D plane strain condition for the analysis. The mechanical energy U of a multi-walled tube under pressure p is a sum of the stretching energies U_M , the bending energy U_B , the interaction energy U_I , and the pressure-induced term Ω . Thus the total potential energy of radially and circumferentially deformed tube under hydrostatic pressure p reads (Shima and Sato 2008)

$$U = U_M + U_B + U_I + \Omega \quad (3)$$

where

$$U_M = \sum_{i=1}^N \frac{\alpha_i a_i^2}{2} \int_0^{2\pi} \left[\frac{v_i' + u_i}{a_i} + \frac{1}{2} \left(\frac{v_i - u_i}{a_i} \right)^2 \right]^2 d\theta \quad (4)$$

$$U_B = \sum_{i=1}^N \frac{\beta_i a_i^4}{2} \int_0^{2\pi} \left(\frac{v_i' - u_i'}{a_i^2} \right)^2 d\theta \quad (5)$$

$$U_I = \sum_{i=1}^{N-1} \left[(1 - \delta_{i,N}) \frac{c_{i,i+1} a_i}{2} \int_0^{2\pi} (u_i - u_{i+1})^2 d\theta + (1 - \delta_{i,1}) \frac{c_{i,i-1} a_i}{2} \int_0^{2\pi} (u_i - u_{i-1})^2 d\theta \right] \quad (6)$$

$$\Omega = p \int_0^{2\pi} \left[u_i a_i + \frac{1}{2} (v_i^2 - u_i' v_i + u_i v_i' + u_i^2) \right] d\theta \quad (7)$$

Here, the two functions $u_i(\theta)$ and $v_i(\theta)$ denote, respectively, the radial and circumferential displacements of a volume element of the i -th tube located at the circumference angle θ . The a_i is the tube radius of the i -th concentric tube, and the following two parameters are employed

$$\alpha_i = \frac{Eh}{(1 - \nu^2)a_i} \quad \text{and} \quad \beta_i = \frac{Eh^3}{12(1 - \nu^2)a_i^3} \quad (8)$$

We use the parameter $E = 1$ TPa as the axial Young modulus of the tube, $\nu = 0.27$ as the Poisson's ratio, $h = 0.34$ nm as the thickness of individual concentric tubes. The van der Waals interaction coefficients $c_{i,j}$ are expressed by

$$c_{i,j} = - \left(\frac{1001 \sigma^{12}}{3D^4} g_{i,j}^{13} - \frac{1120 \sigma^6}{9D^4} g_{i,j}^7 \right) \pi \varepsilon a_j \quad (9)$$

where

$$g_{i,j}^m = \frac{1}{a_i + a_j} \int_0^{2\pi} \frac{1}{\sqrt{1 - b_{i,j} \cos^2 \theta}} d\theta \quad \text{with} \quad b_{i,j} = \frac{4a_i a_j}{(a_i + a_j)^2} \quad (10)$$

and ε and σ are parameters that determine the vdW interaction between two layers ($\varepsilon = 2.968$ meV and $\sigma = 0.3407$ nm)

6.2 Critical pressure for radial deformation

By applying the variation method to the functional $U = U[u_i(\theta), v_i(\theta)]$ given by Eq. (3), we obtain a system of $2N$ differential equations (Shima and Sato 2008):

$$\begin{aligned} & \beta_i (v_i - u_i)'''' - \alpha_i (u_i + v_i)' - \alpha_i \frac{u_i^{(0)}}{a_i} (v_i - u_i)' - \delta_{i,N} p a_N^3 (u_N + v_N)' \\ & + (1 - \delta_{i,N}) c_{i,i+1} a_i (u_i - u_{i+1}) + (1 - \delta_{i,1}) c_{i,i-1} a_i (u_i - u_{i-1}) = 0 \end{aligned} \quad (11)$$

$$\alpha_i(\dot{v}_1 + u_1)' + \beta_i(v_i - u_i)'' - \alpha_i \frac{u_i^{(0)}}{a_i}(v_i - u_i) = 0 \quad (12)$$

Substituting the Fourier series expansions of $u_i(\theta)$ and $v_i(\theta)$:

$$u_i(\theta) = \sum_{k=1}^{\infty} \bar{u}_k^{(i)} \cos k\theta, \text{ and } v_i(\theta) = \sum_{k=1}^{\infty} \bar{v}_k^{(i)} \sin k\theta \quad (13)$$

into Eqs. (11) and (12), we obtain the matrix equation:

$$\mathbf{C}\mathbf{u} = \mathbf{0} \quad (14)$$

where \mathbf{C} is a matrix composed of the coefficients such as $\alpha_i, \beta_i, c_{i,i+1}$, and \mathbf{u} is a vector given by

$$\mathbf{u} = (\dots, \bar{u}_{k-1}^{(i)}, \bar{u}_k^{(i)}, \bar{u}_{k+1}^{(i)}, \dots, \bar{u}_{k-1}^{(i+1)}, \bar{u}_k^{(i+1)}, \bar{u}_{k+1}^{(i+1)}, \dots, \bar{v}_{k-1}^{(i)}, \bar{v}_k^{(i)}, \bar{v}_{k+1}^{(i)}, \dots, \bar{v}_{k-1}^{(i+1)}, \bar{v}_k^{(i+1)}, \bar{v}_{k+1}^{(i+1)}, \dots)^T \quad (15)$$

Then, the secular equation

$$\mathbf{det}(\mathbf{C}) = 0 \quad (16)$$

provides many values of hydrostatic pressure p each of which corresponds to different deformation mode index k defined by Eq. (13). Among these modes, such the mode that gives the minimum value of p is observed at high hydrostatic pressure, and the minimum p serves as the critical pressure above which the cross-sectional shape of a multi-walled nanotube alters from circular to deformed one characterized by a particular value of k .

6.3 Result 1: Cross-sectional shapes under pressure

Fig. 3 gives schematic illustrations of tubes' cross-section under hydrostatic pressure: (a) a circular shape ($k=0$), (b) an elliptically-deformed one ($k=2$), and (c) radially-corrugated one ($k=5$). The innermost tube diameter D is taken to be 6.0 nm for (a) and (b), and 7.0 nm for (c). We see that in the elliptic mode of (b), all constituent shells are radially distorted. On the contrary, in the corrugation mode of (c), only a few outermost shells assume radial deformation while innermost shells keep their cylindrical symmetry. Which kind of deformation mode occurs above p depends on the values of N and D for the multi-walled tube under consideration. We have numerically confirmed that a larger N and a smaller D make corrugation modes with a larger mode-index k be energetically favored.

6.4 Results 2: Critical pressure for radial deformation

Fig. 4 provides critical pressure curves of multi-walled carbon nanotubes composed of N shells with the innermost tube diameter $D = 4.5$ nm. All values of p are estimated to be several GPa, depending on N and D . Given N , such the k -th deformation mode that gives the minimum value of $p(k) \equiv p_c$ is observed above p_c . It follows from the plots that when $N \leq 15$, only an elliptic radial deformation ($k=2$) should be observed. This means that the stable cross-section shape of the tube under pressure higher than p_c is elliptic. When $N \geq 20$, on the other hand, various radial corrugation modes ($k \geq 3$) are possible to occur under hydrostatic pressure at the order of GPa.

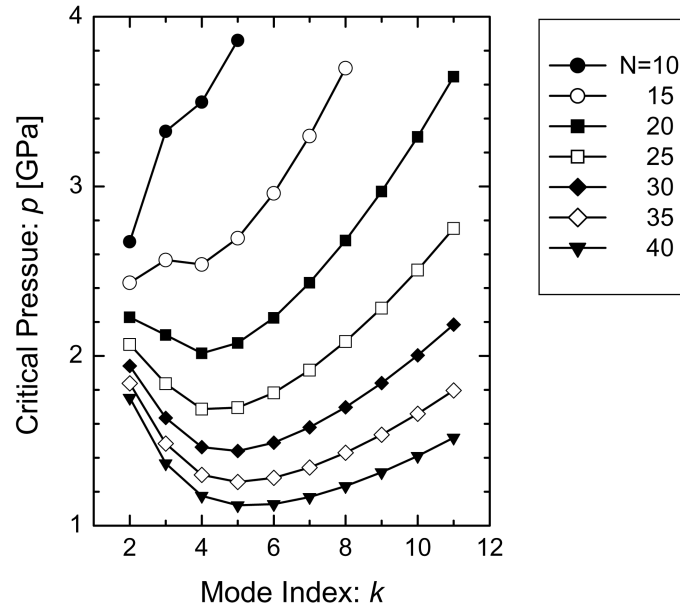


Fig. 4 Critical pressure curves of multi-walled carbon nanotubes composed of N concentric shells. The innermost tube diameter D is fixed to be $D=4.5$ nm. The integer k characterizes radial deformation modes (*i.e.*, stable cross-sectional shapes) of the tubes under high hydrostatic pressure. Given N , such the k -th deformation mode that gives the minimum value of $p(k)$ is observed above. It follows from the plots that when $N \leq 15$, only an elliptic radial deformation ($k=2$) should be observed. When $N \geq 20$, on the other hand, various radial corrugation modes ($k \geq 3$) are possible to occur under hydrostatic pressure at the order of GPa.

7. Carbon nanotube composite materials

As a closing remark, we comment on the utility of carbon nanotubes as reinforcement of various materials (Bal and Samal 2007 and Bredeau *et al.* 2008). Most of the theoretical and experimental results mentioned thus far ensure that carbon nanotubes should be the prime candidate for the next generation of composite filler materials. With this perspective in mind, many researchers are strenuously seeking for applications of nanotubes as filler materials in composite materials. Carbon nanotube fillers are expected not only to improve the mechanical properties of the composite, but also to implement some extra functions such as electric conductivity, thermal conductivity, and electromagnetic shielding. For example, when added to transparent polymers, nanotubes will improve the conductivity without sacrificing much of the transparency of the polymer.

Here are given some recent progress of this issue. Xu *et al.* (2002) have prepared a thin-film epoxy composite that includes 0.1% multi-walled nanotubes as a filler. They have showed that the elastic modulus improves up to 20%. This could be one of the most successful cases, since sometimes we need to add more than 1% to obtain the maximum Young modulus. In general, for the improvement of the Young modulus and the tensile strength in nanotube composites, more than 10% of nanotubes were added (Harris 2004 and Liu *et al.* 2002). In the latter cases, an increased amount of nanotubes in the matrix causes a decrease of the fracture strain; this implies the efficiency of this method for designing materials with desired mechanical characteristics.

Acknowledgements

We acknowledge the support for this research by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan. One of the authors (HS) is thankful for financial supports from the Sumitomo Foundation and the Executive Office of Research Strategy in Hokkaido University.

References

- Arias, I. and Arroyo, M. (2008), "Size-dependent nonlinear elastic scaling of multiwalled carbon nanotubes", *Phys. Rev. Lett.*, **100**, 085503.
- Arroyo, M. and Belytschko, T. (2003), "Nonlinear mechanical response and rippling of thick multiwalled carbon nanotubes", *Phys. Rev. Lett.* **91**, 215505.
- Arroyo, M. and Arias, I. (2008), "Rippling and a phase-transforming mesoscopic model for multiwalled carbon nanotubes", *J. Mech. Phys. Solids*, **56**, 1224-1244.
- Avouris, P., Hertel, T., Martel, R., Schmidt, T., Shea, H. R. and Walkup, R. E. (1999), "Carbon nanotubes: nanomechanics, manipulation, and electronic devices", *Appl. Surface Sci.* **141**, 201-209.
- Bal, S. and Samal, S. S. (2007), "Carbon nanotube reinforced polymer composites - A state of the art", *Bull. Mater. Sci.*, **30**, 379-386.
- Balakrishnan, R. and Dandoloff, R. (2008), "Effect of conformations on charge transport in a thin elastic tube", *Nonlinearity*, **21**, 1-11.
- Batra, R. C. and Sears, A. (2007), "Continuum models of multi-walled carbon nanotubes", *Int. J. Solids. Struct.* **44**, 7577-7596.
- Benedict, L. X., Chopra, N. G., Cohen, M. L., Zettl, A., Louie, S. G. and Crespi, V. H. (1998), "Microscopic determination of the interlayer binding energy in graphite", *Chem. Phys. Lett.* **286**, 490-496.
- Bernholc, J., Brabec, C., Nardelli, M. B., Maiti, A., Roland, C. and Yakobson, B. I. (1998), "Theory of growth and mechanical properties of nanotubes", *Appl. Phys. A*, **67**, 39-46.
- Bredeau, S., Peeterbroeck, S., Bonduel, D., Alexandre, M. and Dubois, P. (2008), "From carbon nanotube coatings to high-performance polymer nanocomposites", *Polym. Int.*, **57**, 547-553.
- Chang, T. C. (2007), "Torsional behavior of chiral single-walled carbon nanotubes is loading direction dependant", *Appl. Phys. Lett.* **90**, 201910.
- Chesnokov, S. A., Nalimova, V. A., Rinzler, A. G., Smalley, R. E. and Fischer, J. E. (1999), "Mechanical energy storage in carbon nanotube springs", *Phys. Rev. Lett.* **82**, 343-346.
- Chopra, N. G., Benedict, L. X., Crespi, V. H., Cohen, M. L., Louie, S. G. and Zettl, A. (1995), "Fully collapsed carbon nanotubes", *Nature*, **377**, 135-138.
- Christofilos, D., Arvanitidis, J., Kourouklis, G. A., Ves, S., Takenobu, T., Iwasa, Y. and Kataura, H. (2007), "Identification of inner and outer shells of double-wall carbon nanotubes using high-pressure Raman spectroscopy", *Phys. Rev. B*, **76**, 113402.
- Demczyk, B. G., Wang, Y. M., Cumings, J., Hetman, M., Han, W., Zettl, A. and Ritchie, O. (2002), "Direct mechanical measurement of the tensile strength and elastic modulus of multiwalled carbon nanotubes", *Mater. Sci. Eng. A*, **334**, 173-178.
- Despres, J. F., Daguere, E. and Lafdi, K. (1995), "Flexibility of graphene layers in carbon nanotubes", *Carbon*, **33**, 87-89.
- Elliott, J. A., Sandler, J. K. W., Windle, A. H., Young, R. J. and Shaffer, M. S. P. (2004), "Collapse of single-wall carbon nanotubes is diameter dependent", *Phys. Rev. Lett.* **92**, 095501.
- Frackowiak, E. and Beguin, R. (2001), "Carbon materials for the electrochemical storage of energy in capacitors", *Carbon*, **39**, 937-950.
- Frackowiak, E. and Beguin, R. (2002), "Electrochemical storage of energy in carbon nanotubes and nanostructured carbons", *Carbon*, **40**, 1775-1787.
- Gadagkar, V., Maiti, P. K., Lansac, Y., Jagota, A. and Sood, A. K. (2006), "Collapse of double-walled carbon

- nanotubes bundles under hydrostatic pressure”, *Phys. Rev. B*, **73**, 085402.
- Gao, G. H., Cagin, T. and Goddard, W. A. (1998), “Energetics, structure mechanical and vibrational properties of single-walled carbon nanotubes”, *Nanotechnology*, **9**, 184-191.
- Harris, P. J. F. (2004), “Carbon nanotube composites”, *Int. Mater. Rev.*, **49**, 31-43.
- Hasegawa, M. and Nishidate, K. (2006), “Radial deformation and stability of single-wall carbon nanotubes under hydrostatic pressure”, *Phys. Rev. B*, **74**, 115401.
- Hernandez, E., Goze, C., Bernier, P. and Rubio, A. (1998), “Elastic Properties of C and BxCyNz composite nanotubes”, *Phys. Rev. Lett.*, **80**, 4502-4505.
- Hertel, T., Walkup, R. E. and Avouris, P. (1998), “Deformation of carbon nanotubes by surface van der Waals forces”, *Phys. Rev. B* **58**, 13870-13873.
- Iijima, S. (1991), “Helical microtubules of graphitic carbon”, *Nature*, **354**, 56-58.
- Iijima, S., Brabec, C., Maiti, A. and Bernholc, J. (1996), “Structural flexibility of carbon nanotubes”, *J. Chem. Phys.* **104**, 2089-2092.
- Jensen, K., Mickelson, W., Kis, A. and Zettl, A. (2007), “Buckling and kinking force measurements on individual multiwalled carbon nanotubes”, *Phys. Rev. B*, **76**, 195436.
- Khosravian, N. and Rafii-Tabar, H. (2007), “Computational modelling of the flow of viscous fluids in carbon nanotubes”, *J. Phys. D* **40**, 7046-7052.
- Khosravian, N. and Rafii-Tabar, H. (2008), “Computational modelling of a non-viscous fluid flow in a multi-walled carbon nanotube modelled as a Timoshenko beam”, *Nanotechnology*, **19**, 275703.
- Kowalczyk, P., Holyst, R., Terrones, M. and Terrones, H. (2007), “Hydrogen storage in nanoporous carbon materials: myth and facts”, *Phys. Chem. Chem. Phys.*, **9**, 1786-1792.
- Li, C. and Chou, T. W. (2003), “A structural mechanics approach for the analysis of carbon nanotubes”, *Int. J. Solids Struct.* **40**, 2487-2499.
- Li, X. F., Wang, B. L. and Mai, Y. W. (2008), “Effects of a surrounding elastic medium on flexural waves propagating in carbon nanotubes via nonlocal elasticity”, *J. Appl. Phys.* **103**, 074309.
- Liu, T., Phang, I., Shen, L., Chow, S. and Zhang, W. (2004), “Morphology and mechanical properties of multiwalled carbon nanotubes reinforced nylon-6 composites”, *Macromolecules*, **37**, 7214.
- Lopez, M. J., Rubio, A., Alonso, J. A., Qin, L. C. and Iijima, S. (2001), “Novelpolygonized single-wall carbon nanotube bundles”, *Phys. Rev. Lett.*, **86**, 3056-3059.
- Lordi, V. and Yao, N. (1998), “Radial compression and controlled cutting of carbon nanotubes”, *J. Chem. Phys.* **109**, 2509-2512.
- Lu, J. P. (1997), “Elastic properties of carbon nanotubes and nanoropes”, *Phys. Rev. Lett.*, **79**, 1297-1300.
- Majumder, M., Chopra, N., Andrews, R. and Hinds, B. J. (2005), “Nanoscale hydrodynamics - Enhanced flow in carbon nanotubes”, *Nature*, **438**, 44-44.
- Nardelli, M. B., Yakobson, B. I. and Bernholc, J. (1998), “Mechanism of strain release in carbon nanotubes”, *Phys. Rev. B*, **57**, 4277-4280.
- Natsuki, T. and Endo, M. (2004), “Stress simulation of carbon nanotubes in tension and compression”, *Carbon*, **42**, 2147-2151.
- Natsuki, T., Tantrakarn, K. and Endo, M. (2004a), “Effects of carbon nanotube structures on mechanical properties”, *Appl. Phys. A*, **79**, 117-124.
- Natsuki, T., Tantrakarn, K. and Endo, M. (2004b), “Prediction of elastic properties for single-walled carbon nanotubes”, *Carbon*, **42**, 39-45.
- Nishio, T., Miyato, Y., Kobayashi, K., Matsushige, K. and Yamada, H. (2008), “Piezoresistive properties of carbon nanotubes under radial force investigated by atomic force microscopy”, *Appl. Phys. Lett.* **92**, 063117.
- Noy, A., Park, H. G., Fornasiero, F., Holt, J. K., Grigoropoulos, C. P. and Bakajin, O. (2007), “Nanofluidics in carbon nanotubes”, *Nano Today*, **2**, 22-29.
- Ono, S. and Shima, H. (2009), “Tuning the electrical resistivity of semiconductor thin films by nanoscale corrugation”, *Phys. Rev. B*, **79**, 235407.
- Onoe, J., Ito, T., Shin-ishi, K., Ohno, K., Noguchi, Y. and Ueda, S. (2007), “Valence electronic structure of cross-linked C-60 polymers: In situ high-resolution photoelectron spectroscopic and density-functional studies”, *Phys. Rev. B*, **75**, 233410.
- Overney, G., Zhang, W. and Tomanek, D. (1993), “Structural rigidity and low-frequency vibrational-modes of

- long carbon tubes”, *Z. Phys. D*, **27**, 93-96.
- Peters, M. J., McNeil, L. E., Lu, J. P. and Kahn, D. (2000), “Structural phase transition in carbon nanotube bundles under pressure”, *Phys. Rev. B*, **61**, 5939-5944.
- Poncharal, P., Wang, Z. L., Ugarte, D. and de Heer W. A. (1999), “Electrostatic deflections and electromechanical resonances of carbon nanotubes”, *Science*, **283**, 1513-1516.
- Qian, D., Liu, W. K., Subramoney, S. and Ruoff, R. S. (2003), “Effect of interlayer potential on mechanical deformation of multiwalled carbon nanotubes”, *J. Nanosci. Nanotechnol.*, **3**, 185-191.
- Reich, S., Thomsen, C. and Ordejon, P. (2002), “Elastic properties of carbon nanotubes under hydrostatic pressure”, *Phys. Rev. B*, **65**, 153407.
- Reich, S., Thomsen, C. and Ordejon, P. (2003), “Elastic properties and pressure-induced phase transitions of single-walled carbon nanotubes”, *Phys. Stat. Solid. B*, **235**, 354-359.
- Rols, S., Gontcharenko, I. N., Almairac, R., Sauvajol, J. L. and Mirebeau, I. (2001), “Polygonization of single-wall carbon nanotube bundles under high pressure”, *Phys. Rev. B*, **64**, 153401.
- Ruoff, R. S. and Lorents, D. C. (1995), “Mechanical and thermal-properties of carbon nanotubes”, *Carbon*, **33**(7), 925-930.
- Ruoff, R. S., Tersoff, J., Lorents, D. C., Subramoney, S. and Chan, B. (1993), “Radial deformation of carbon nanotubes by Van-der-Waals forces”, *Nature*, **364**, 514-516.
- Sharma, S. M., Karmakar, S., Sikka, S. K., Teredesai, P. V., Sood, A. K., Govindaraj, A. and Rao, C. N. R. (2001), “Pressure-induced phase transformation and structural resilience of single-wall carbon nanotube bundles”, *Phys. Rev. B*, **63**, 205417.
- She, W., Jiang, B., Han, B. S. and Xie, S. S. (2000), “Investigation of the radial compression of carbon nanotubes with a scanning probe microscope”, *Phys. Rev. Lett.*, **84**, 3634-3637.
- Shima, H. and Sato, M. (2008), “Multiple radial corrugations in multiwalled carbon nanotubes under pressure”, *Nanotechnology*, **19**, 495705.
- Shima, H. and Sato, M. (2009), “Pressure-induced structural transitions in multi-walled carbon nanotubes”, *Physica Status Solidi (a)*, in press; arXiv:0905.4145.
- Shima, H., Yoshioka, H. and Onoe, J. (2009), “Geometry-driven shift in the Tomonaga-Luttinger exponent of deformed cylinders”, *Phys. Rev. B*, **79**, 201401.
- Sun, C. and Liu, K. (2008), “Combined torsional buckling of multi-walled carbon nanotubes coupling with axial loading and radial pressures”, *Int. J. Solids. Struct.*, **45**, 2128-2139.
- Taira, H. and Shima, H. (2007), “Curvature effects on surface electron states in ballistic nanostructures”, *Surface Science*, **601**, 5270-5275.
- Taira, H. and Shima, H. “Torsion-induced persistent current in a twisted quantum ring”, submitted; arXiv: 0904.3149.
- Tang, D. S., Bao, Z. X., Wang, L. J., Chen, L. C., Sun, L. F., Liu, Z. Q., Zhou, W. Y. and Xie, S. S. (2000), “The electrical behavior of carbon nanotubes under high pressure”, *J. Phys. Chem. Solids*, **61**, 1175-1178.
- Tang, J., Qin, L. C., Sasaki, T., Yudasaka, M., Matsushita, A. and Iijima, S. (2000), “Compressibility and polygonization of single-walled carbon nanotubes under hydrostatic pressure”, *Phys. Rev. Lett.*, **85**, 1887-1889.
- Tang, J., Qin, L. C., Sasaki, T., Yudasaka, M., Matsushita, A. and Iijima, S. (2002), “Revealing properties of single-walled carbon nanotubes under high pressure”, *J. Phys. Condens. Matt.*, **14**, 10575-10578.
- Tangney, P., Capaz, R. B., Spataru, C. D., Cohen, M. L. and Louie, S. G. (2005), “Structural transformations of carbon nanotubes under hydrostatic pressure”, *Nano Lett.*, **5**, 2268-2273.
- Tersoff, J. and Ruoff, R. S. (1994), “Structural properties of a carbon-nanotube crystal”, *Phys. Rev. Lett.*, **73**, 676-679.
- Toda, Y., Ryuzaki, S. and Onoe, J. (2008), “Femtosecond carrier dynamics in electron-beam-irradiated C-60 film”, *Appl. Phys. Lett.*, **92**, 094102.
- Treacy, M. M. J., Ebbesen, T. W. and Gibson, J. M. (1996), “Exceptionally high Young’s modulus observed for individual carbon nanotubes”, *Nature*, **381**, 678-680.
- Wang, C. Y., Ru, C. Q. and Mioduchowski, A. (2003), “Elastic buckling of multiwall carbon nanotubes under high pressure”, *J. Nanosci. Nanotechnol.*, **3**, 199-208.
- Wang, C. Y., Zhang, C. M., Wang, C. M. and Tan, V. B. C. (2007), “Buckling of carbon nanotubes: A literature survey”, *J. Nanosci. Nanotechnol.*, **7**, 4221-4247.

- Whitby, M. and Quirke, N. (2007), "Fluid flow in carbon nanotubes and nanopipes", *Nature Nanotechnol.* **2**, 87-94.
- White, C. T., Robertson, D. H. and Mintmire, J. W. (1993), "Helical and rotational symmetries of nanoscale graphitic tubules", *Phys. Rev. B*, **47**, 5485-5488.
- Wong, E. W., Sheehan, P. E. and Lieber, C. M. (1997), "Nanobeam mechanics: Elasticity, strength, and toughness of nanorods and nanotubes", *Science*, **277**, 1971-1975.
- Xu, X., Thwe, M. M., Shearwood, C. and Liao, K. (2002), "Mechanical properties and interfacial characteristics of carbon-nanotube-reinforced epoxy thin films", *Appl. Phys. Lett.* **81**, 2833-2835.
- Yang, X., Wu, G. and Dong, J. (2006), "Structural transformations of double-walled carbon nanotubes bundle under hydrostatic pressure", *Appl. Phys. Lett.*, **89**, 113101.
- Yakobson, B. I., Brabec, C. J. and Bernholc, J. (1996), "Nanomechanics of carbon tubes: Instabilities beyond linear response", *Phys. Rev. Lett.*, **76**, 2511-2514.
- Yakobson, B. J. and Smalley, R. E. (1997), "Fullerene nanotubes: C-1000000 and beyond", *Am. Sci.*, **85**, 324-337.
- Yu, M. F., Kowalewski, T. and Ruoff, R. S. (2000), "Investigation of the radial deformability of individual carbon nanotubes under controlled indentation force", *Phys. Rev. Lett.* **85**, 1456-1459.
- Yu, M. F., Dyer, M. J. and Ruoff, R. S. (2001a), "Structure and mechanical flexibility of carbon nanotube ribbons: An atomic-force microscopy study", *J. Appl. Phys.* **89**, 4554-4557.
- Yu, M. F., Kowalewski, T. and Ruoff, R. S. (2001b), "Structural analysis of collapsed, and twisted and collapsed, multiwalled carbon nanotubes by atomic force microscopy", *Phys. Rev. Lett.* **86**, 87-90.
- Zhang, S., Khare, R., Belytschko, T., Hsia, K. J., Mielke, S. L. and Schatz, G. C. (2006), "Transition states and minimum energy pathways for the collapse of carbon nanotubes", *Phys. Rev. B*, **73**, 075423.